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RECENT ADVANCES IN CERAMIC MATERIALS
APPLICABLE IN SPACE TECHNOLOGY

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RECENT ADVANCES IN CERAMIC MATERIALS APPLICABLE IN SPACE TECHNOLOGY **/1

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Various composite materials for use in space technology are reviewed, including sandwich constructions, composite ceramic foams, formed and unformed ceramic glazings, with and without thermoplastic and thermosetting resin binders, with and without lightening agents, whisker reinforcements, etc. Work done at Thomson-Houston on increasing the effective protection period of ceramics for re-entry cones, leading edges of ailerons, linings for duct throats, etc. showed that the addition of organic or mineral pellets, silica fibers, and endothermal materials resulted in an extension of the effective protection period to 350 sec at a surface heat of 2500° C and a cold zone of about 200° C. Further increase in this period is expected by combination of various heat barriers and addition of endothermal materials superior to NH_4Cl. author

INTRODUCTION

For applications in space structures where the following properties are required: high melting point, extreme hardness, good thermal insulation, and chemical inertia at elevated temperatures, it appears that ceramic materials are the most satisfactory. Because of their intrinsic properties, ceramic materials

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** Numbers in the margin indicate pagination in the original foreign text.

are very often misjudged and somewhat disregarded, being considered as miracle materials by some and systematically rejected by others. The term "ceramic" primarily includes objects shaped from oxides (silicates, argils, etc.) and then any compound with ionic bonds, predominantly characterized by great fragility, absence of ductility, and high resistance to ordinary temperature. In this paper, we will only consider materials having a fusion point above 2000°C. In addition, we will discuss only silica fibers despite their low melting point, because of their interesting mechanical properties and the facility of their industrial-scale manufacture. Graphite, metals, and their alloys (even inter-metallic compounds) will be excluded.

The first part of the paper gives a brief review of the physico-chemical properties of the main ceramic types that might be useful in space technology. The second part describes the various classes of products and their fields of /2 application, while the third part is devoted to composite ceramic materials and to our experimental contribution in this particular field.

I. PHYSICO-CHEMICAL PROPERTIES

The ceramic materials of interest here are compounds of the following metalloids: oxygen, boron, carbon, nitrogen, silicon with the transition metals and the elements of Group IV B. These materials are characterized by a very high lattice energy, which is responsible for their properties. The interatomic bond is primarily ionic and four property classes are differentiated for these materials:

1) Thermal;

2) Mechanical;

3) Electrical;

4) Chemical.

For these four classes, the thermal factor is the one that influences these properties and gives them their specific interest. Finally, from the structural viewpoint, these solids always are encountered in the form of compact stacks or piles. We will successively investigate these four property classes for a certain number of ceramic materials; this particular list is not restrictive and concerns only compounds of technical as well as of economical interest.

I.1 Thermal Properties

The thermal constants of several ceramic types are compiled in Table I. These values concern only dense single-phase and well-defined materials. For a given development, it is possible to modify certain properties such as the heat conductivity or the density. These facts will be discussed further in the second part of this paper. The Table indicates the wide range of the heat conductivity and density values of these bodies.

I.2 Mechanical Properties

At ordinary temperature, the mechanical properties of ceramics are characterized by high cohesion, great fragility, and extreme hardness. Nevertheless, the interest in the mechanical properties of these materials is ruled by the temperature, for which reason we have entered primarily the mechanothermal properties in Table II.

I.2.1 Expansion Coefficient 13

The mean order of magnitude of this value is located near 7×10^{-6} cm/^{o}C cm. Nevertheless, certain ceramic materials are in existence whose coefficient is

TABLE I

Materials	Fusion Point	Specific Heat cal/gm	Heat Conductivity 20°C	Heat Conductivity 1000°C cal/°C/sec/cm	Density gm/cm^3
ThO_2	3,050°C	0.06	0.10	0.008	10.03
MgO	2,800°C	0.21	0.1	0.02	3.58
ZrO_2	2,700°C	0.11	0.046	0.004	5.6
BeO	2,550°C	0.260	0.6	0.05	3.01
Al_2O_3	2,050°C	0.174	0.12	0.016	3.96
HfC	3,900°C				11.0
TaC	3,850°C	0.04	0.07	0.030	13.2
ZrC	3,500°C	0.07	0.09		6.1
B_4C	2,450°C	0.228			2.3
TiC	2,400°C	0.13	0.12	0.015	4.1
SiC	2,350°C	0.16	0.49	0.05	3.0
HfN	3,300°C				13.8
B N	3,000°C	0.11	0.07	0.035	2.1
ZrN	2,800°C	0.07	0.07	0.015	7.3
ZrB_2	2,900°C		0.055		5.7
TiB_2	2,850°C				4.2

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TABLE II

Material	Knoop Hardness kg/mm^2	Expansion Coefficient $\times 10^{-6}$ °C	Elasticity Modulus kg/mm^2
B_4C	2,750	4.5	
SiC	2,480		
TiC	2,470	7.42	32,200
Al_2O_3	2,100	7.2	35,800
ZrC	2,100	6.73	38,800
TaC	2,000	6.29	29,100
Wc	1,880		
TiN	1,800		
ZrB_2	1,550	6.83	35,000
B_2O	1,250		
ZrO_2	1,160	8.6	17,500
ZrN	1,480		

/2b

lower, specifically ceramics that have a helicoidal structure, such as β-quartz. Thus, the expansion coefficient is zero for spodumene, for β-eucryptite, and for glass 9 SiO_2, TiO_2. The coefficient is close to $0.5 \times 10^{-6}/^{\circ}C$ for aluminum titanate. Unfortunately, all these compounds, with the exception of Al_2O_3 and TiO_2, are very little refractory. Overall, the thermal expansion of ceramics is less than that of metals.

I.2.2 Resistance to Thermal Shocks

The concept of thermal shock is directly connected with the fragility of ceramic materials. This resistance can be expressed by a simple relation, as follows:

$$R = \frac{TK}{\alpha E}$$

where

R = resistance to thermal shocks (number);

T = tensile strength;

K = heat conductivity;

α = expansion coefficient;

E = elasticity modulus.

In Table III, the values of R are given for several ceramics. In general, a ceramic is sensitive to temperature fluctuations when located in the domain of spontaneous fracture without having passed through a plastic domain, as a function of the load applied. Conversely, at high temperatures, a ceramic is ductile and is only little affected by variations in temperature. It should be mentioned that the value of R depends on the manufacturing method and on the state of compactness of the ceramic (influence on T and K).

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TABLE III

Materials	Tensile Strength	Heat Conductivity	Electricity Modulus	Expansion Coefficient	Thermal Resistance
ThO_2	1,000 kg/cm^2	0.10	25,100	10.5×10^{-6}	4 000
ZrO_2	1,500 kg/cm^2	0.04	17,500	8.6×10^{-6}	4 000
Al_2O_3	2,700 kg/cm^2	0.12	35,800	7.2×10^{-6}	12,600

I.2.3 Hardness

Hardness is a property specific to ceramic materials (except for diamonds) which is due to their great structural cohesion.

In Table II, the hardness values for several ceramics are given. No other /4 material reaches similar values, except some intermetallic compounds which resemble ceramic materials in some of their mechanical properties. This characteristic permits their use as abrasive materials and in any field in which resistance to abrasion and erosion is required.

I.2.4 Development of these Properties as a Function of Temperature

By measuring the creep at high temperatures, the behavior under load can be measured. For ceramics on a 96% fritted dense alumina base, a creep value of 2% is reached only at 1800°C at a stress of 2 kg/cm². This property is affected by the chemical purity of the material and by the chemical nature of the environment. For comparison purposes, even refractory metals have a compressive strength of zero at this temperature.

I.3 Electrical Properties

Boron oxides and nitrides have an extremely high electric resistivity, close to 10^5 to 10^{12} Ω/cm. Conversely, insertion ceramics such as borides or carbides are semiconductors or have metallic conductivity. It should be mentioned that the electric conductivity is influenced by the content of impurities and the chemical composition of the gaseous environment.

The oxides present a high dielectric strength and a loss angle which is a function of the compacting. Finally, a rise in temperature makes ceramic materials lose their insulating character, at least changing them into a semiconductor type. The only exception is boron nitride which preserves its insulating character even at very high temperatures.

I.4 Chemical Properties

For possible application in astronautics, ceramics have the following three properties:

Resistance to gaseous environment;

Compatibility with metals;

Chemical inertia.

I.4.1 Resistance to Gaseous Environment /5

Thorium, zirconium, and aluminum oxides (for example) are the only compounds that, in air, are able to resist a temperature above 2000° C. Conversely, the carbides, nitrides, and borides are able to exist in a reducing or carburizing atmosphere above 2000° C. These latter compounds are thermally more refractory than the oxides. Their great hardness makes them resistant to erosion produced by solids in suspension within combustion gases. Table IV gives a compilation of the resistance to oxidation, as a function of the temperature, for various ceramics.

I.4.2 Compatibility with Adjacent Structures

Because of the very large free energy of formation, ceramic materials can be placed next to metals without fear of interaction. So as to maintain this compatibility up to as high as possible a temperature, the ceramic material must be as compact as possible. Consequently, a ceramic can be used as the core in a

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TABLE IV

Materials	Type of Resistance to Oxidation	Legend
Al, Be Oxides	1	Class 1 : Oxidation resistance 1,700°C
SiC	2	
TiB_2	2 - 3	" 2 : " between 1,400 - 1,700°C
ZrB_2	2 - 3	
B_4C	3	" 3 : " " 1,100 - 1,400°C
TiC	3	
ZrC	3	" 4 : " " 800 - 1,100°C
TaC	3	
ZrN	3	" 5 : " " 500 - 800°C
B N	3	
HfN	3	

sandwich construction between two materials that are not compatible in themselves.

I.4.3 Chemical Inertia

The great stability of ultrarefractory ceramic materials gives them a considerable inertia to acid or basic reagents. Finally, in a high vacuum, even at extreme temperatures, the ceramic materials show no vapor tension (except for decomposing materials).

II. INVESTIGATION OF FIELDS OF APPLICATION FOR CERAMIC MATERIALS AS A FUNCTION OF THEIR TREATMENT

According to the AFNOR and PRE Standards, ceramic materials are subdivided into two classes:

formed;

unformed.

The first category includes all products that have been shaped or formed before heat treatment, while the second group contains all products that were given their final form only after firing.

II.1 Formed Ceramics /6

Only products that may be of use in space technology will be discussed here. These formed materials can be used in the compact or lightened state, depending on the required missions.

II.1.1 Compact Products

These materials have the following properties: thermal refractoriness, mechanical strength at high temperatures, chemical inertia. These properties reach a maximum when the densification attains the theoretical value. Ceramics on a carbon base have the following advantages, at equivalent refractoriness:

Greater hardness, resulting in increased resistance to erosive agents;

Compatibility with oxidizing or corrosive gases (depending on the selected type).

Present or scheduled applications for these products are as follows:

Turbine blades of compact ceramics with a high thermal shock resistance;

Convergent part of ducts.

Mechanical parts exposed to high stresses at elevated temperatures (also at ambient temperature) or to intense abrasion such as, for example, crossbars, bearings, axles.

Leading edges, subject to excessive temperature rise.

The selected ceramics may be either oxides or insertion compounds (carbides, nitrides, etc.) manufactured in such a manner as to eliminate all porosity. After heat treatment, a blank is obtained which, in the given case, can be converted to the wanted dimensions. Progress in the past few years has consisted mainly in the manufacture of such ultrarefractory ceramics, with a high degree of compactness, and in perfecting their conversion.

II.1.2 Lightened Products /7

The purpose for such cellular materials is the following: thermal (or also acoustic) insulation, and decrease in structural load. Such products are obtained in micro- or macrocellular form. They are being manufactured by three different processes: combustion of a finely divided charge at the interior of the refractory matrix; mixing of a ceramic slip with a foam; filling a plastic resin foam with ceramic powder. The heat treatment is the same as for the compact products. Depending on the manufacturing process, products with open or closed porosity, with various dimensions of the honeycomb, are obtained. The interpore space can be either microcellular or dense, depending on the intended purpose. Thus, it is possible to obtain ceramics with apparent densities 5 - 10 times less than the theoretical value; under these conditions, aluminum oxide foams have an apparent density of 0.5 gm/cm^3.

The applications for cellular refractories with communicating voids are basically composite materials with resin impregnation (see Part III). Conversely, the materials of the second type can be used as replacement of compact ceramics if the load is to be reduced. Because of the excellent densification of the intercellular space, their resistance to erosion is equivalent to the compact products.

Conclusion

Because of the considerable progress made in the development of shaped refractory products, it is possible to expect the following performances:

Light-weight material, great hardness, resistance to erosion.

Thermal insulation or good heat conductivity (depending on the selection of material) and dimensional stability, even after protracted use under extreme conditions.

Another fairly important property of ceramic materials is the low cost of raw materials which, in addition, are available on the national scale. Their conversion requires classical forms and dies, at investments that are not excessive.

II.2 Unformed Ceramics /8

The products in this category require no shaping equipment and assume the shape of the object they are to protect. We will successively investigate the following:

Enamels.

Glazings on a binder base.

Coatings obtained by vacuum deposition or by projection.

II.2.1 Enamels

To increase the life of certain elements used in aeronautics, their walls are enameled. An enamel is a ceramic substance with preponderant vitreous phase and a low fusion point. The function is to provide thermal and chemical protection, for example, for conduits subject to corrosion by combustion gases. Unfortunately, because of their low refractoriness, enamels have found only restricted use in space technology.

II.2.2 Glazings

Refractory fire clays can be prepared by mixing a ceramic powder with a binder. Such a binder produces a chemical or hydraulic set at room temperature, giving the product a certain cohesion. Fire clays of this type have been used as leading edges or for interconnecting certain structural elements. Their use does not seem widespread in space structures.

II.2.3 Refractory Coatings obtained by

Projection.

Deposition in the gaseous phase.

II.2.3.1 Projection of Refractory Powders

To protect structural elements, refractory powders can be "projected" by means of an oxyhydrogen blowpipe or a plasma blowtorch. The powder is melted by passing it through the flame of the blowpipe and is projected, in the molten state, onto the surface to be protected. This produces a porous coating of a rather low density, permitting excellent thermal insulation. The work-up is 19
simple and permits treatment of parts of any shape.

II.2.3.2 Vapor Deposition

The most general method for depositing ceramic materials consists in decomposing a halide in the presence of a gaseous metalloid, on a preheated support. This heated support forms the focus of decomposition and deposition. This results in a dense coating of wanted thickness, well adapted to the support. The method permits preparing ceramic coatings of no matter what material, within a temperature interval quite below the maximum operative temperature. Unfortunately, this technique requires rather complex equipment and a highly delicate conversion.

In fact, aluminum oxide deposition is done by careful hydrolysis of the aluminum chloride. To obtain a homogeneous deposition without porosity, while still maintaining excellent adherence to the support, the following parameters must be mastered:

Temperature of the support, partial pressures of the various gaseous constituents.

Chemical nature of the transport gas, kinetics of the reaction.

For protection in oxidizing atmospheres, a deposition of zirconium and magnesium oxide is in question (to stabilize the cubic phase). Conversely, a satisfactory coating for neutral or reducing atmospheres would be zirconium carbide.

Conclusion

Unformed ceramic materials, because of their diversity of work-up, permit a protection from heat, corrosion, and erosion of parts of complicated shape and given dimensions. Above, we discussed the various possibilities of work-up of ceramic materials used without additions; however, for space missions their /10 performance characteristics are not sufficient. In fact, the materials must have rather contradictory properties, such as extremely light weight, low heat conductivity, chemical inertia under extreme thermal fluxes over long periods of time. To meet these requirements, research and development people have developed composite ceramic materials.

III. COMPOSITE CERAMIC MATERIALS

Introduction

To meet the contradictory requirements made on materials for space application, solutions that simultaneously satisfy these conditions had to be developed. These include: extremely extensive thermal fluxes at high temperatures; highly erosive and corrosive environments; abrupt variations in temperature and pressure. In addition, because of the new missions of future rockets, stipulations for their useful life have changed from a few seconds to one hour. Table V gives a compilation of the most recent conditions made on materials used as deflectors for rocket engines and for re-entry cones.

The thermal protection must be efficient under conditions of the following types of heat transfer:

TABLE V

Conditions	Rocket Launchers		Re-entry Cones
	Actual	Projected	
Temperature °C	3,000	5,000	8,000
Thermal flux cal/cm^2 sec	800	1,500	2,500
Duration, sec	60	3,600	10-500
Type of gas	Neutral to highly corrosive		

/10a

a) By conduction (specifically in the region close to the structure to be protected).

b) By convection (of turbulent gas jets issuing from the ducts).

c) By radiation of solids (including suspensoids in the exhaust gases).

d) By radiation of gases.

In addition, the coating or the structural element must be able to resist high thermal shocks and stresses of thermal origin. In fact, the surface temperature of the material increases rapidly to 2500 - 3000°C while the interior only reaches temperatures of 100 - 200°C at relatively low thickness (a few centimeters).

This transient state takes place on combustion cutoff and re-ignition /11 during a given mission. In addition, a structural element must retain its state and shape for the entire duration of the mission, which may be as high as 60 min (for example, in gliding flight).

III.1 General Solutions

The primary means for obtaining such thermal protection in space was the use of composite materials: organic resins with a highly ablative effect, reinforced with mineral fibers (glass or silica). Unfortunately, these materials had a useful life limited to a few seconds and a low resistance to erosion; in addition, the resultant layer of porous carbon showed extremely low cohesion.

The protective characteristics to be exhibited by a composite material are as follows:

1) High heat absorption, by conversion of the substances with endothermal effect and by liberation of a large volume of gas, so as to produce sweat cooling on the surface of the material.

2) Formation of a refractory top coating, in accordance with:

heat trap;

insulating refractory.

3) Excellent mechanical strength, permitting satisfactory behavior under thermal shock and under abrasion or erosion by the combustion gases.

a) <u>Absorption of Heat by Endothermal and Transpiration Effects</u>

Substances of this type have the function of heat dissipation, specifically during the transient regime. The materials are added to the skeleton of the coating and play the role of heat barriers. During the entire time of their thermodynamic transition (fusion, sublimation, phase change), these substances maintain the coating at the given temperature, because of the endothermal concomitant effect. Table VII lists the substances with the highest transition enthalpies, of potential usefulness in this particular technology. By proper selection of endothermal-effect materials, undergoing transition at different /12 temperatures, it is possible to obtain a series of heat barriers. In addition, it will be necessary to incorporate, into the coating matrix, endothermal substances that sublime at the transition point. The liberated gases will permit cooling of the surface by transpiration.

b) <u>Final Protection by Refractory Coatings</u>

As soon as the transient regime has been entered, a final protection up to the end of the mission must be provided. This can be conveniently obtained by refractory materials constituting the skeleton of the composite material. If this protection is effected by a heat trap, the material must have a high heat capacity and high thermal conductivity as well as the highest possible fusion

/11a

TABLE VI

Substance	Transition Point	Heat of Transition
AlN	2,000°C	3,680 cal/gm
Si_3N_4	1,900°C	2,780
Mg_3N_2	1,500°C	2,110
NH_4F	400°C	1,270
Nylon	350°C	1,070
NH_4Cl	335°C	985
AlF_3	1,270°C	900
KCNO	700°C	880
CdO	900°C	687
ZnO	1,800°C	550
Na_2O	1,275°C	550
Teflon	730°C	440
GeO	710°C	435

point. In this case, the best ceramics, in order, are the following: SiC, BeO, BN, TiN, MgO, TiC.

Conversely, if the coating is to be of the insulating type, the material must have a very high fusion point, a very low thermal conductivity, even at high temperatures, and a good behavior under thermal shock. The best materials, again in order, are the following: ThO_2, TiC, ZrN, TiN, MgO, TaC, BN.

c) Improvement of Mechanical Properties

Since the mechanical strength of ceramic materials is insufficient when subjected to high stresses within very short periods of time, this strength must be increased by the use of reinforcements. Fibrous materials such as silica fibers, glass or graphite fibers, and refractory metals have a high elasticity which permits a softening of the composite materials. This whiskers reinforcement is efficient only if it retains its fibrous state. The tensile strength of polycrystalline silica fibers is of the order of 4000 kg/cm^2 while that of zirconium is 14,000 kg/cm^2.

A combination of these three solutions makes it possible to obtain composite ceramics which, in formed or unformed shapes, represent materials of excellent performance.

III.2 Composite Ceramics /13

Two types of composite ceramics have found application in space technology:

composite foams;

unformed coatings.

Other arrangements are well possible but the two above main types have given the most interesting results.

III.2.1 Composite Ceramic Foams

Such materials are composed of a skeleton shaped as a honeycomb refractory, manufactured in accordance with the method described in Chapter II.1.2. After machining and putting into final form, this ceramic foam is impregnated with organic resins (phenolics, phenylsilanes, polyethylenes, or polyamides). The ceramic material itself must be as light and coherent as possible. Experimental results have shown that phenolic and phenylsilane resins act as structural reinforcements and as heat barriers. Conversely, thermoplastic resins destroy the honeycomb structure during polymerization. To avoid this deterioration, the foams are impregnated with a mixture of thermosetting and thermoplastic resins. Table VII contains the characteristics of the principal presently available foams.

Materials of this type are intended for applications in which a long-time thermal protection, at absolute dimensional stability, is required. After extraction of the organic resins, the refractory foam has the function of an insulator whose ablation is effected after its fusion. To reduce the rate of ablation, refractories with viscous fusion should be selected. Experiments made with aluminum and zirconium foams, impregnated with epoxyphenolic resins, have shown that, to bring the cold surface to a temperature of 300°, ten minutes were required with the former and twenty-two minutes with the latter material. The thickness of the specimens was 3 cm, while the apparent density of the aluminum foam was 1.05 and that of the zirconium foam was 1.45 $\%/m^3$.

Applications in question are primarily for re-entry cones of manned capsules and any other problem requiring an efficient heat shield for prolonged periods /14 of time, at absolute dimensional stability.

TABLE VII

Substance	F.P. %	Porosity %	Density ρ gm/cm^3	At 350°C Heat Conductivity k	$\rho k \cdot 10^{-6}$	Compressive Strength
SiO_2	1,720	84	0.34	0.0037	125	50 kg/cm^2
Al_2O_3	2,050	88	0.52	0.0140	720	70
ZrO_2	2,700	86	0.73	0.0032	220	20
SiC	2,350	90	0.32	0.0198	635	14

/13a

III.2.2 Unformed Composite Ceramic Materials

Two types of composite glazings have been developed:

organic matrix, loaded with ceramic powders;

ceramic matrix, loaded with plastic resin powders.

The first of these glazings has been specifically investigated by the ONERA (National Aerospace Research and Development Administration) and is composed of a phenolic resin matrix (or other type), loaded with a mixture of basic oxides and aluminum (or zirconium) powders.

After removing the plastic resin by ablation, the boron oxide produces first a fritting, followed by a vesiculation under formation of a boro-alumina glass. Finally, by raising the temperature, the boron oxide is driven off, leaving a cellular alumina coating. These coatings, which are formed during the mission itself, have given interesting results as heat shields for various powder rocket engines.

Glazings of the second type have been experimentally investigated by us and will be described in the following Chapter.

III.3 Work at Thomson-Houston on Development of a High-Performance Composite Ceramic Glazing

Introduction

To obtain information of ablative materials as heat shields for space structures, we concentrated our study on composite glazings on a ceramic base. So as to increase the period of effective protection to a maximum, we incorporated all types of heat barriers into this material, including insulation, enthalpy of endothermal transition, anisotropic heat conductivity for dissipating the calories parallel to the surface to be protected. Reinforcement of /15 the material is obtained by incorporation of mineral fibers, while its lightening is produced by low-density spherules.

III.3.1 Experimental Setup

III.3.1.1 Preparation

The specimens for this study were parallelepipeds of 5 × 10 cm surface and about 1 cm thickness. The matrix of our materials was a mixture of aluminum or zirconium oxide bonded with "Astroceram" R cement. This cement keeps its entire mechanical cohesion up to sintering of the oxide powder. The following materials are incorporated into this matrix:

a) Fibrous whiskers (SiO_2, ZrO_2, carbon).

b) Lightening agents (alumina or polystyrene pellets).

c) Agents of endothermal effect (see Table VI).

Lightening by means of hollow bubbles yields an excellent thermal insulation at very high temperatures. To obtain a series of heat barriers, it is preferable to incorporate an entire range of endothermal agents. Finally, a sheet casting of low thickness permits an orientation of the whiskers in a plane perpendicular to the thermal flux.

III.3.1.2 Experiments

The period of effective protection of these materials from thermal flux is measured in the following manner: A specimen with the above dimensions is rapidly introduced into a plasma flame, to within 20 mm from the core. A considerable thermoelectric current will osculate its cold wall.

By definition, the life of the heat shield is determined from the time required to bring the cold surface to a temperature of 200° C. This temperature of 200° C was selected since it apparently constitutes a critical value, still permitting satisfactory operation of the structure. Figure 1 shows the investigation of a facing specimen. /16

III.3.2 Results

III.3.2.1 Influence of the Content in Lightening Materials

Elongation of the above composite materials is obtained by incorporation of corundum or polystyrene pellets into the refractory matrix. Their optimum diameter is located between 0.5 and 1.0 mm, for reasons of cohesion and heat conductivity. The volumetric weight of the ceramic pellets is about 1 kg while for the organic pellets it is about 10 gm. The results plotted in Fig.2 refer only to refractory cements on an alumina and zirconium base, into which these pellets are encapsuled in various proportions. Figure 2 shows the variation in the life of the heat shield (see Sect.III.3.1.2), as a function of the pellet content, together with the density for the same products. The curves indicate the following:

a) The period of effective protection depends directly on the pellet concentrations.

b) This period is longer, at equal pellet content, for a material with a lower heat conductivity (ZrO_2) with respect to Al_2O_3.

c) The density decreases with increasing pellet concentration.

So as to decrease the density of the facing furthermore, without substantial loss of cohesion, we investigated mixtures of mineral and organic pellets. These results are plotted in Fig.3; despite a considerable decrease in density with increasing content of organic pellets, no noticeable lengthening of the heat shield life was observed.

III.3.2.2 Influence of the Content in Silica Fibers /17

The addition of silica fibers has the double purpose of increasing the mechanical strength and of decreasing the heat conductivity. In this case, silica whiskers were incorporated into the refractory matrix by mastication. Figure 4 shows the evolution of the effective protection period as a function of the fiber concentration.

The following was observed:

Approximately linear increase in life of the heat shield, as a function of the fiber concentration.

Simultaneous decrease in density.

Longer effective protection with a zirconium matrix than with an alumina matrix.

Under these conditions, it was possible to obtain a facing with an effective life of 230 sec. By the addition of pellets, this period was brought to 350 sec per centimeter of coating.

III.3.2.3 Influence of Endothermal Substances

Substances with an endothermal effect, studied by us, include ammonium chloride and a phenolic resin which were incorporated into refractory matrices (aluminum oxide).

Figure 5 shows the evolution of the effective protection period as a function of their concentration. This period is longer with ammonium chloride than with phenolic resin. A good heat barrier is obtained with traces of moisture, provided that bursting of the material is avoided. Figure 6 shows an ordinary piece of sheet metal of 2 mm thickness, one portion of which had been given a protective coating while the other was left uncoated.

Two zones of this sheet were placed into the flame of a 12-kw plasma blow-torch. To make a hole in the unprotected zone, 2 min were required while it took 22 min to produce a hole in the protected zone.

III.3.2.4 Conclusion

/18

The first experiments on developing a composite ceramic facing showed the favorable effect of additions of organic and mineral pellets, silica fibers, and endothermal substances. At present, a life of the heat shield of 350 sec has been obtained for a surface at more than 2500° C and a cold zone not exceeding 200° C.

This protective period can be increased readily by combining various heat barriers and by adding endothermal materials superior to NH_4Cl. The lightening can be further perfected by using microporous chamottes which might result in densities of the order of 0.8 gm/cm^3. This latter lightening simultaneously will permit a reduction in the weight of the necessary coating and in its thickness for a given protection period. Finally, the use of whiskers (SiO_2, ZrO_2, graphite, TiN) of high quality will contribute to an improvement in the mechanical properties.

IV. GENERAL CONCLUSIONS

The above review has defined the progress obtained in the field of manufacturing ceramic materials and their possible applications in space technology. The basic properties of such materials are as follows:

High fusion point.

Extreme hardness combined with an excessive but surmountable fragility.

Good or poor heat transfer.

Chemical composition up to elevated temperatures.

It is the wide range of available ceramics that is responsible for the diversity of the frequently contradictory properties. In addition, the development of composite materials on a ceramic base has made it possible to obtain the following characteristics:

Greater resistance to thermal shock. /19

Reduction of the heat transfer, compared to conventional ceramics.

Reduction in density without loss in mechanical strength.

The possible application fields for ceramics in space structures include the following:

re-entry cones;

leading edges for ailerons;

convergent section of ducts;

protection of the divergent section of ducts;

barrier zones between duct throat and adjacent structure;

mechanical parts, required to withstand high temperatures, strong abrasion, and corrosive environment.

From the time that ceramic materials no longer were restricted to products on a clay base until today, there has been considerable progress in their manufacture and development, permitting numerous applications in all advanced technologies.

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APPENDIX /20

Legend for the various illustrations of the Paper presented by Schmitt.

Fig.1 - Specimen of Composite Material during Tests in a Plasma Blowtorch

Fig.2 - Curves for the Effective Protection Period of a Composite Material, as a Function of the Concentration in Refractory Alumina and Zirconium Pellets

Fig.3 - Curves for the Effective Protection Period of a Composite Material, as a Function of the Concentration in Mineral and Organic Pellets

Fig.4 - Curves for the Effective Protection Period of a Composite Material, as a Function of the Concentration in Silica Fibers Incorporated into Alumina and Zirconium Matrices

Fig.5 - Curves for the Effective Protection Period of a Composite Material, as a Function of the NH_4Cl and Phenolic Resin Content

Fig.6 - Aluminum Sheet Exposed to a Plasma Flame in the Unprotected and Protected Zone

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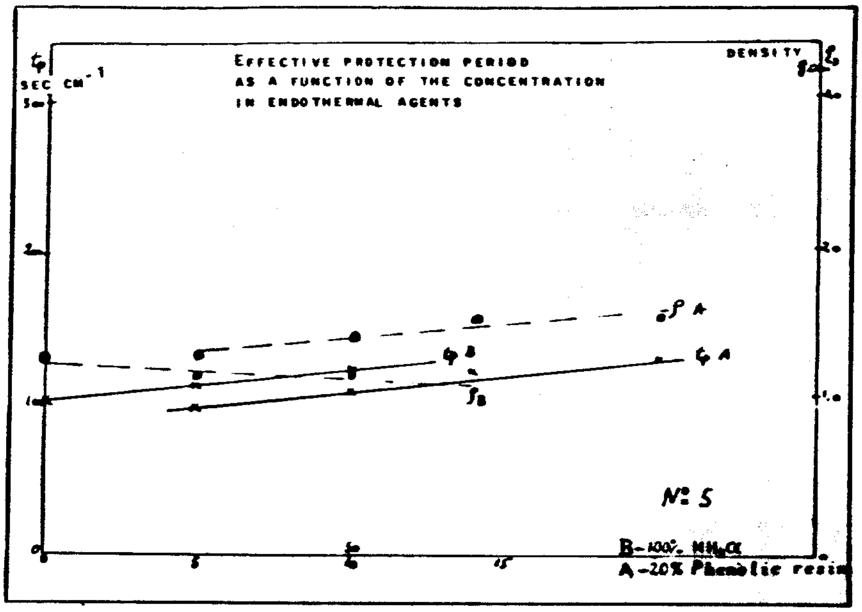

EFFECTIVE PROTECTION PERIOD
AS A FUNCTION OF THE CONCENTRATION
IN ENDOTHERMAL AGENTS
SEC CM^{-1}
DENSITY
N° 5
B-100% NH_4Cl
A-20% Phenolic resin

Fig.5

Fig.6

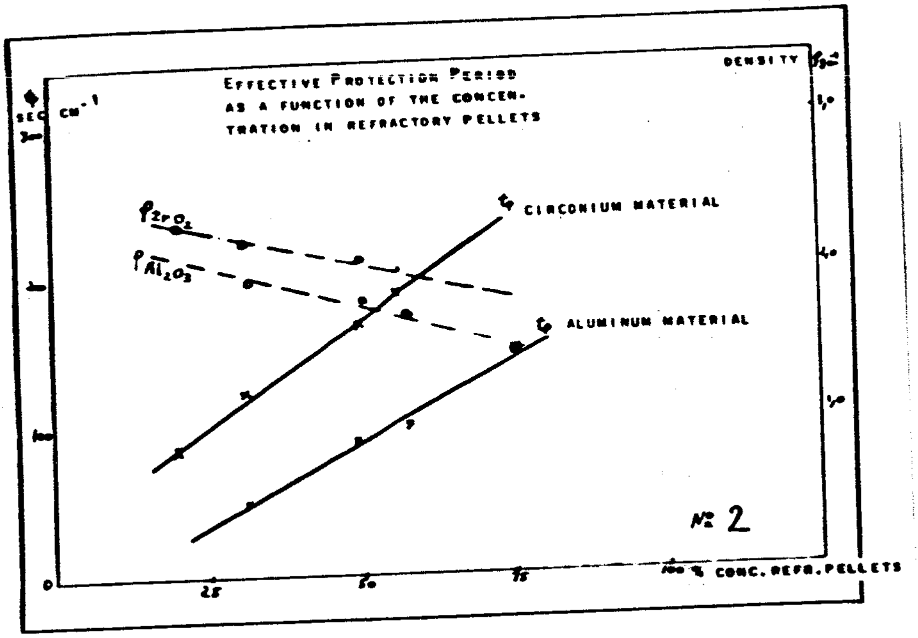
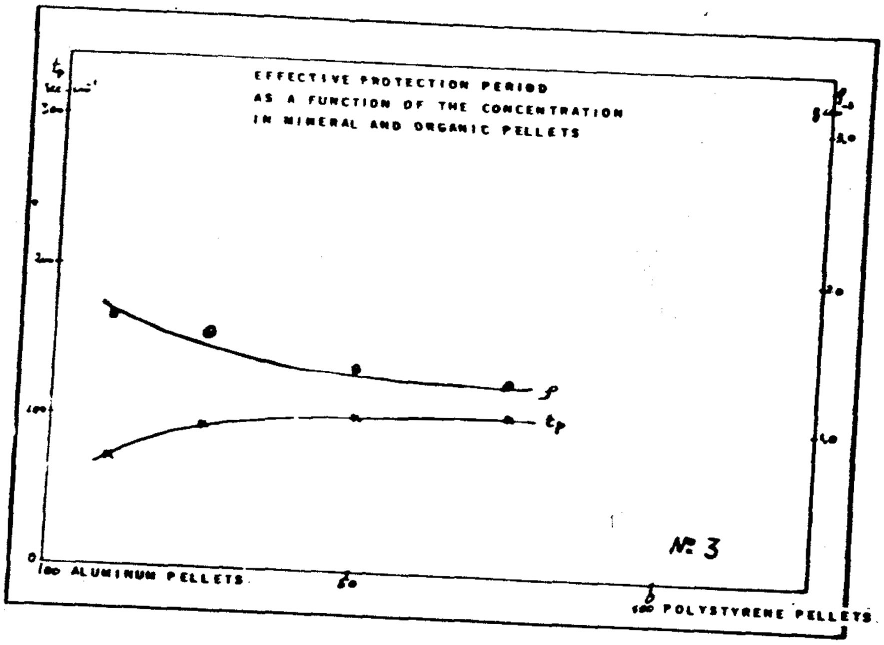

EFFECTIVE PROTECTION PERIOD
AS A FUNCTION OF THE CONCEN-
TRATION IN REFRACTORY PELLETS
DENSITY
SEC CM^{-1}
ρ_{ZrO_2}
$\rho_{Al_2O_3}$
CIRCONIUM MATERIAL
ALUMINUM MATERIAL
№ 2
0
25
50
75
100 % CONC. REFR. PELLETS

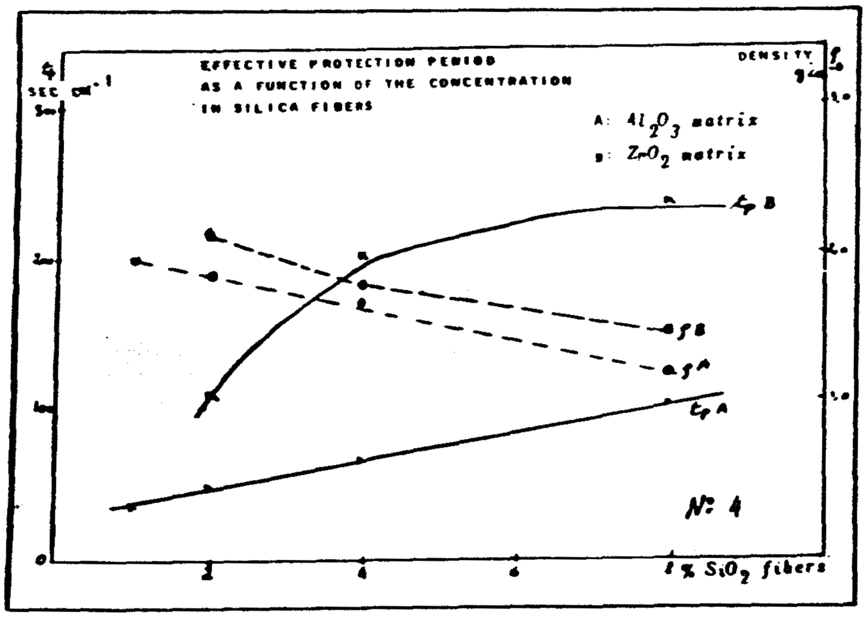
Fig.1

Fig.2



EFFECTIVE PROTECTION PERIOD
AS A FUNCTION OF THE CONCENTRATION
IN MINERAL AND ORGANIC PELLETS
ρ
t_p
№ 3
0
100 ALUMINUM PELLETS
50
0
100 POLYSTYRENE PELLETS

Fig.3



EFFECTIVE PROTECTION PERIOD
AS A FUNCTION OF THE CONCENTRATION
IN SILICA FIBERS
DENSITY
SEC CM^{-1}
A: Al_2O_3 matrix
B: ZrO_2 matrix
t_p B
ρ B
ρ A
t_p A
№ 4
0
2
4
6
8 % SiO_2 fibers

Fig.4